# Case Study - Monitored Natural Attenuation program for benzene cleanup within a 'reasonable timeframe'

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# Outline

- Site History
- Original Site Conceptual Model
  - MNA wouldn't achieve cleanup objective
- Revised Site Conceptual Model
  - MNA could achieve cleanup objective
- Evaluation of Conceptual Model with field data
- Monitored Natural Attenuation Program

# Refinery/Terminal - Site History

- 1920 to 1965 - 180 acre site operated by Pure Oil Company as petroleum refinery.
- 1965 - Acquired by Unocal during Pure Oil merger.
- 1970 - Facility sold to second company to be operated as tank farm and fuel terminal only.
- Present - 75 to 100 acres still operational as fuel terminal.

# History of Environmental Impacts

- 1970 - Product seeps into creek approximately 3,000 feet downgradient from site. 8,000 gallons of product recovered by Coast Guard.
- 1972 to 1981 - Approximately 430,000 gallons of product recovered from wells drilled by State EPA and USEPA.
- 1990 - USEPA mandated interceptor trench along creek. No product recovered since trench installation.

# History of Environmental Investigations

- 1991 - State sues companies. Companies enter into Consent Order to conduct site investigation.
- 1993 to 1997 - Subsurface investigation & risk assessment.
- 1999 - State lawsuit pending depending on remediation effort undertaken by companies.

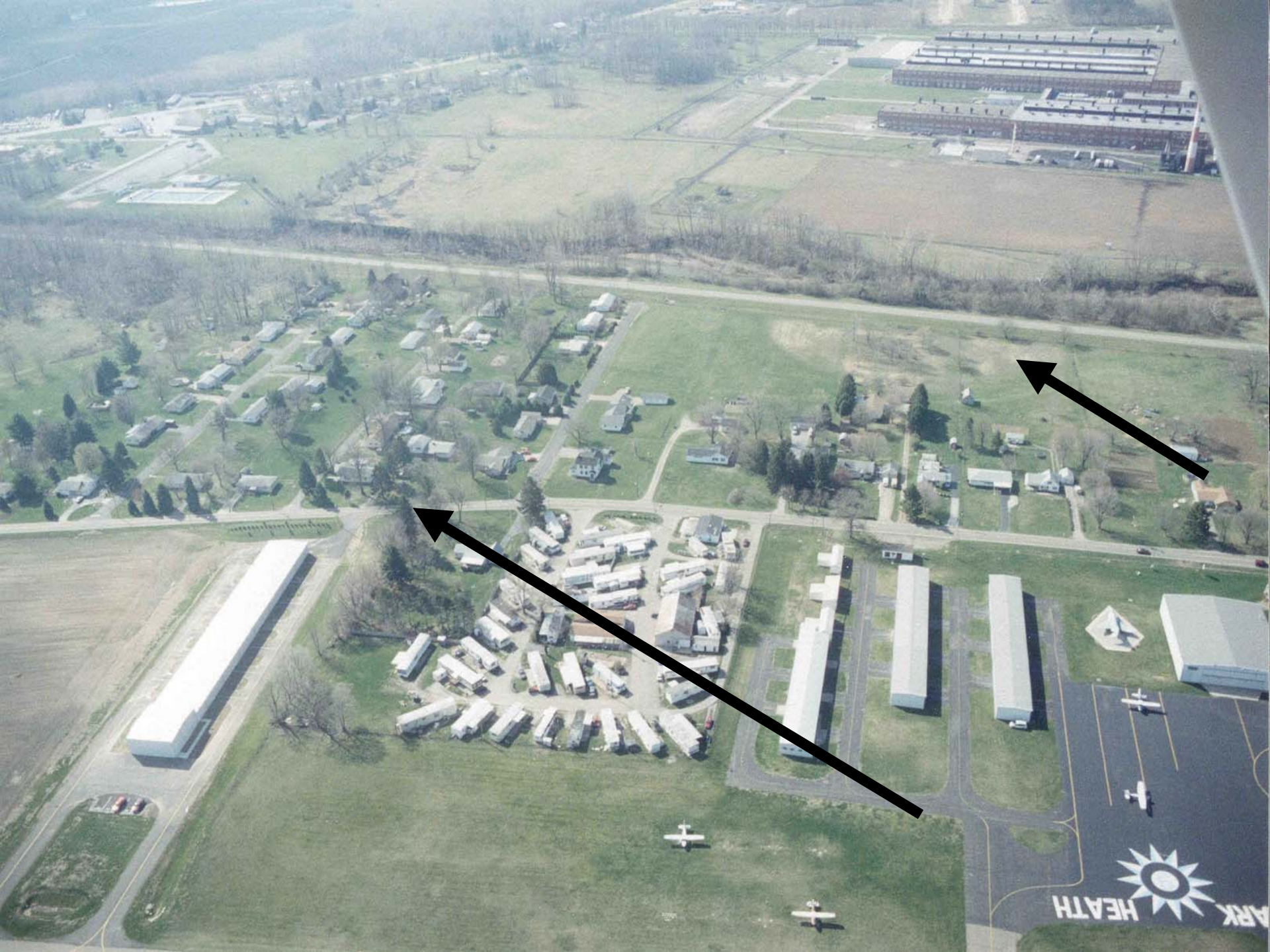
**Objective - cleanup groundwater so that wells in residential area can be used <u>within reasonable timeframe</u>**

# Original Site Conceptual Model

- Product is gasoline (1/3) & diesel (2/3) mix - transported offsite as separate phase on groundwater - remaining product exists in smear zone above and below top of groundwater.
- Technical Expert #1 estimates > 3,600 years to remove benzene from vadose zone - percolation water model.
- Technical Expert #2 estimates > 800 years to remove benzene from groundwater - fate and transport model.
- Groundwater in residential area would <u>not</u> be cleaned up within a reasonable time frame.

# Revised Conceptual Model

- Technical expert #1 overestimated time frame for removing benzene from vadose zone due to incorrect input of site parameters. Technical expert #1 subsequently agreed that benzene in vadose zone could be removed in reasonable time frame.
- Technical expert #2 overestimated time frame for removing benzene from groundwater because loss of benzene due to biodegradation in source area was not included in model. State EPA agreed that benzene could be removed in reasonable time frame due to additional biodegradation.


HEATH

# Vadose Zone Model revised on basis of input parameters

**Calculation of benzene removal rate from unsaturated soil by dissolution into percolation water**

| Parameter | Expert | Site Data | Units | Comments |
|---|---|---|---|---|
| **percolation water** | 8 | 8 | inches/year | regional rate for percolation |
| **thickness** | 8 | 9 | feet | smear zone in vadose zone |
| **TPH** | 130,000 | 4,650 | ppm | |
| **benzene** | 2 | 0.6 | %-TPH | fresh gasoline @ 2% B |
| **toluene** | 8 | 2.4 | %-TPH | fresh gasoline @ 8% T |
| **ethylbenzene** | 2 | 0.6 | %-TPH | fresh gasoline @ 2% E |
| **xylenes** | 9 | 2.7 | %-TPH | fresh gasoline @ 9% X |
| **porosity** | 0 | 0.3 | | gas-filled porosity |
| **soil density** | 2.09 | 2.6 | gm/cc | 2.6 gm/cc typical for soil |
| | | | | |
| **benzene** | 700 | 1780 | mg/L | pure component solubility |
| **toluene** | 512 | 512 | mg/L | pure component solubility |
| **ethylbenzene** | 180 | 180 | mg/L | pure component solubility |
| **xylenes** | 170 | 170 | mg/L | pure component solubility |
| | | | | |
| **Rate Removal from Vadose Zone (infinite source transport model)** | | | | |
| **benzene** | 0.339 | 0.258 | gm/sq.ft. | rate added to aquifer / year |
| **toluene** | 0.840 | 0.252 | gm/sq.ft. | rate added to aquifer / year |
| **ethylbenzene** | 0.064 | 0.019 | gm/sq.ft. | rate added to aquifer / year |
| **xylenes** | 0.272 | 0.082 | gm/sq.ft. | rate added to aquifer / year |
| | | | | |
| **Benzene Cleanup** | **3633** | **50** | **years** | |
| | | | | |
| **Benzene** | **5** | **2 to 4** | **mg/L** | test of model - predicted benzene concentration in groundwater |

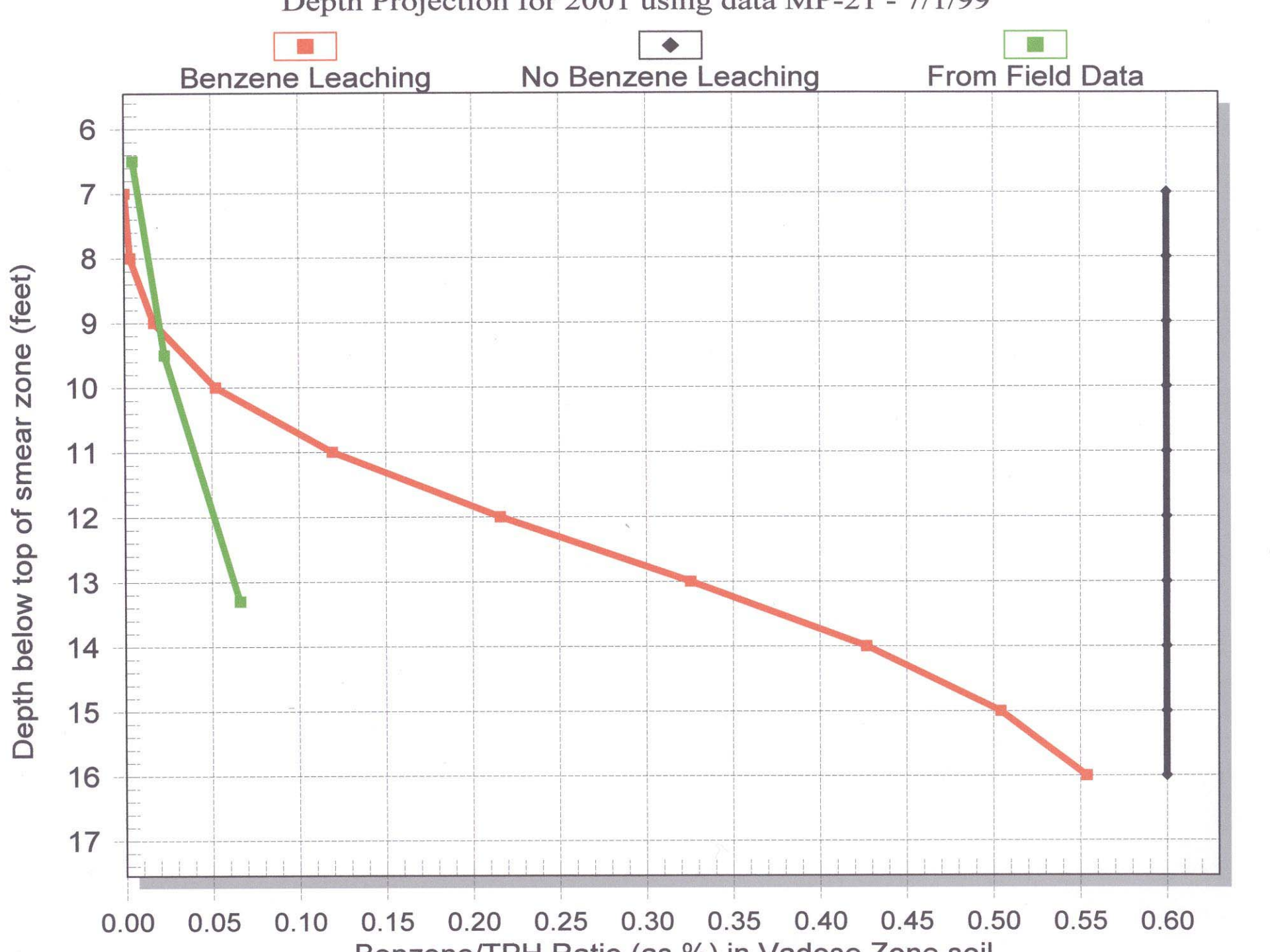
| Initial concentration in soil | | |
|---|---|---|
| **Expert** | **Site Data** | **Units** |
| 1231.0 | 12.9 | B - gm/sq.ft. |
| 4924.0 | 51.8 | T - gm/sq.ft. |
| 1231.0 | 12.9 | E - gm/sq.ft. |
| 5539.5 | 58.2 | X - gm/sq.ft. |

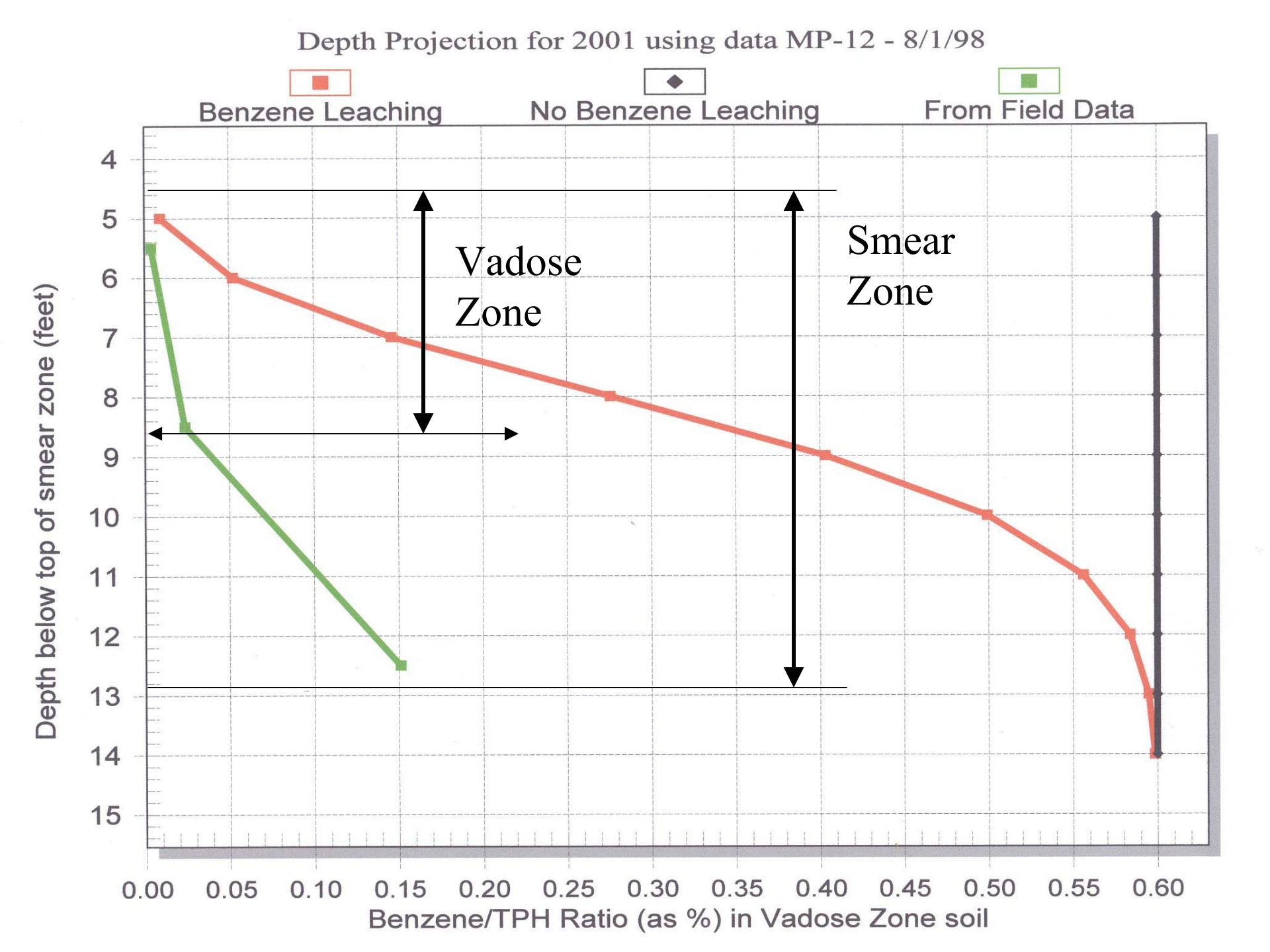
**Expert estimated benzene concentration in gw from mixing model - groundwater flow and percolation water flow**

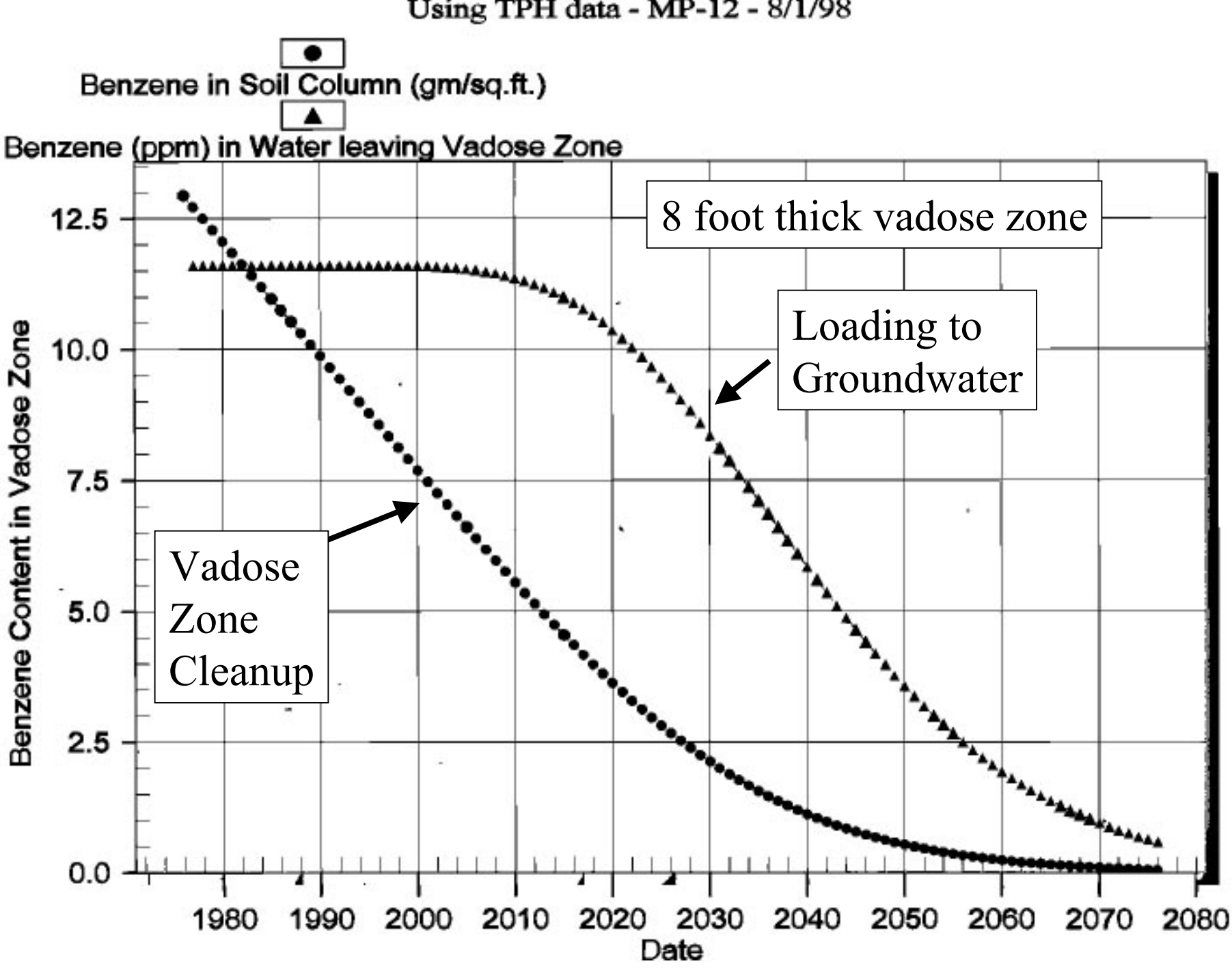
**Site Model - benzene concentration in gw not result of mixing but partitioning from TPH in saturate smear zone**

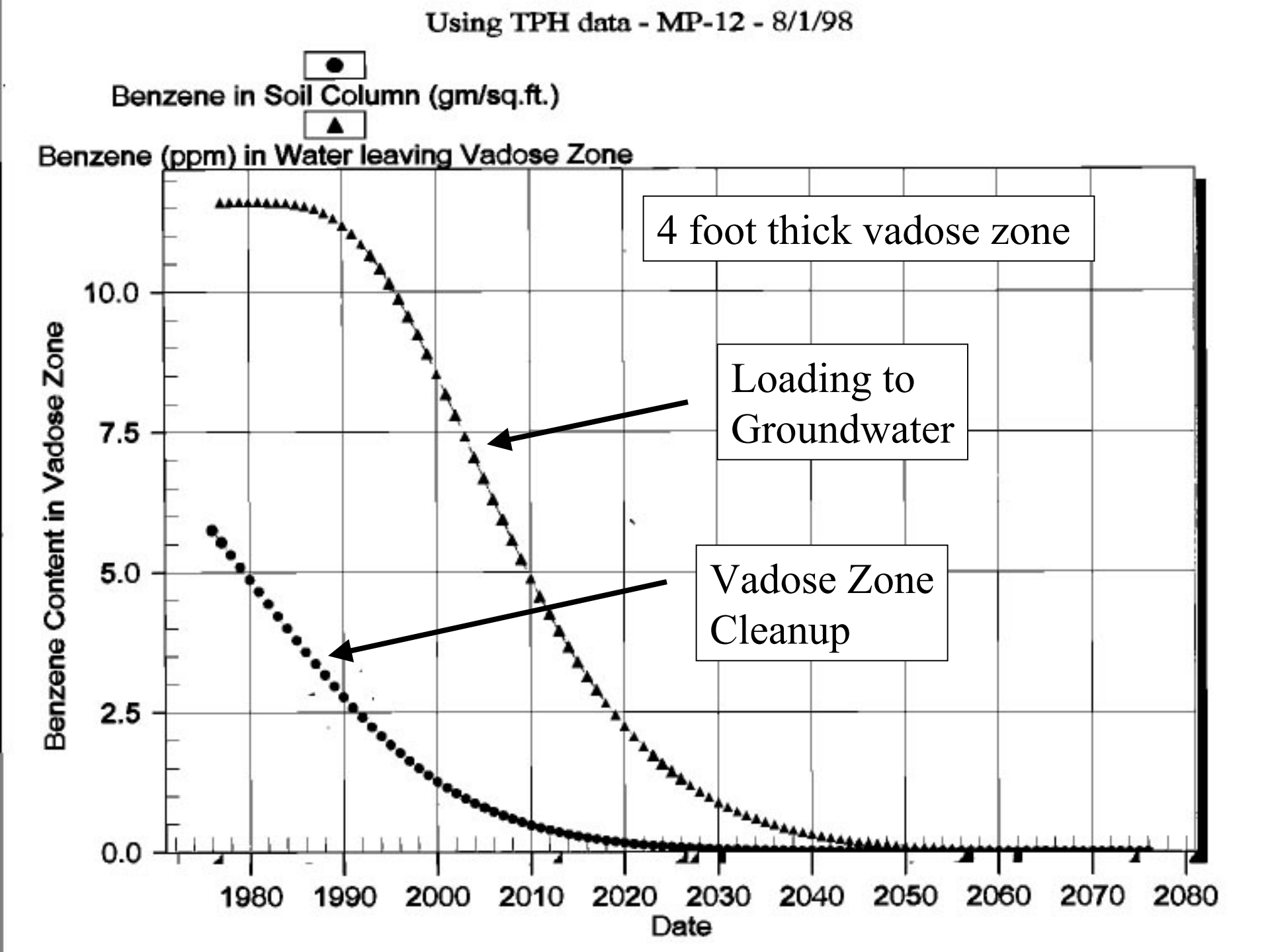
# Field Test Percolation Water Model

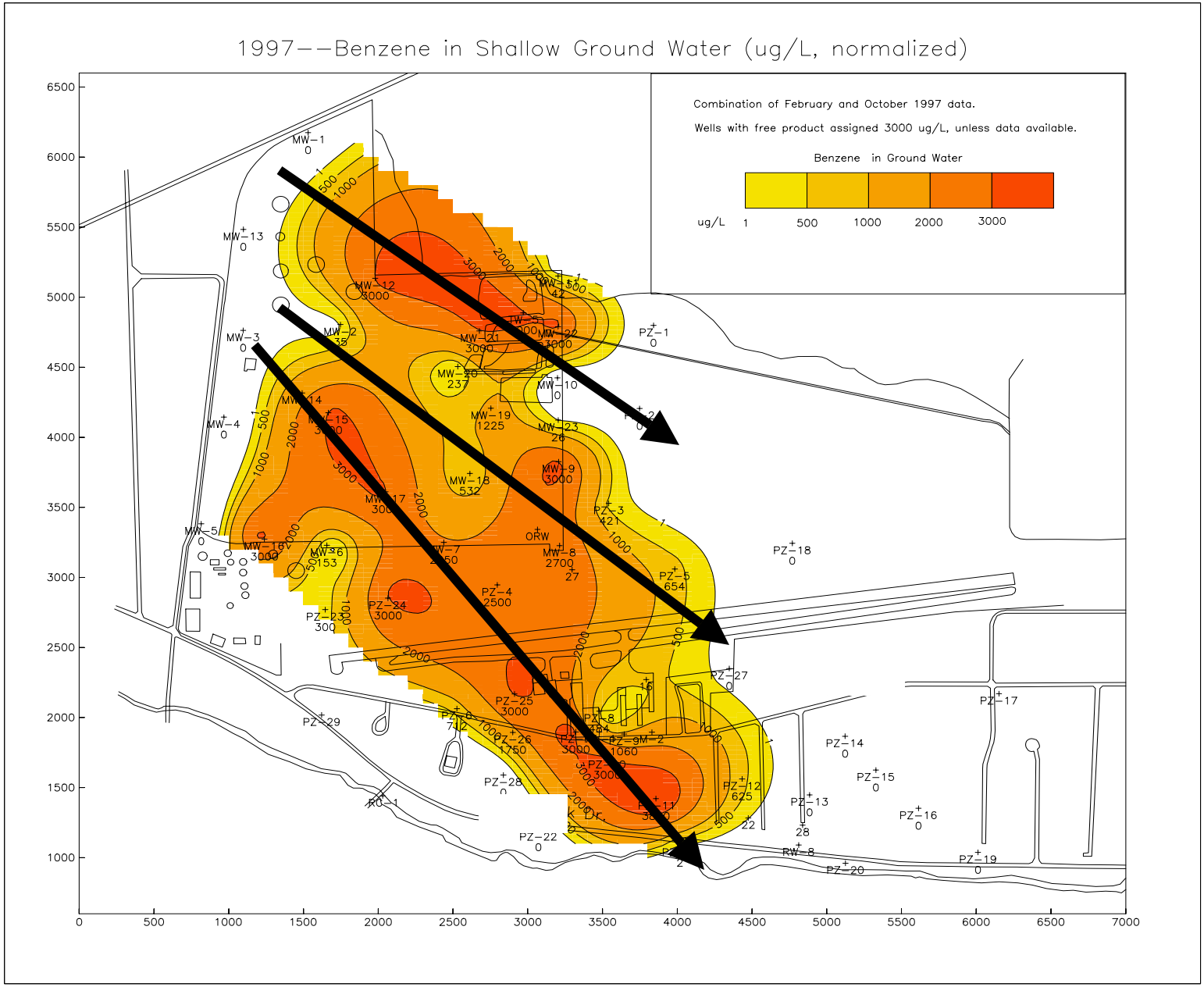
- Modify State leaching model for benzene (after VLEACH)
  - Calculated depth profile of benzene & benzene/TPH at given times since leaching began (1976)
- Compared B/TPH profiles projected by model to those determined from field data for 64 borings collected 1997-2001
  - Model TPH value for 1976 = maximum field measurement for boring.
  - Model B/TPH value for 1976 = 0.6% - based on gasoline/diesel ratio.
- B/TPH profiles for 64 borings
  - Model and field data showed preferential leaching at top of smear zone.
  - In general, less benzene in smear zone than model predicts.


Depth Projection for 2001 using data MP-21 - 7/1/99
Benzene Leaching
No Benzene Leaching
From Field Data
Depth below top of smear zone (feet)
6
7
8
9
10
11
12
13
14
15
16
17
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60


Depth Projection for 2001 using data MP-12 - 8/1/98
Benzene Leaching
No Benzene Leaching
From Field Data
Vadose Zone
Smear Zone
Depth below top of smear zone (feet)
4
5
6
7
8
9
10
11
12
13
14
15
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
Benzene/TPH Ratio (as %) in Vadose Zone soil


Using TPH data - MP-12 - 8/1/98
Benzene in Soil Column (gm/sq.ft.)
Benzene (ppm) in Water leaving Vadose Zone
8 foot thick vadose zone
Loading to Groundwater
Vadose Zone Cleanup
Benzene Content in Vadose Zone
12.5
10.0
7.5
5.0
2.5
0.0
1980
1990
2000
2010
2020
2030
2040
2050
2060
2070
2080
Date


Using TPH data - MP-12 - 8/1/98
Benzene in Soil Column (gm/sq.ft.)
Benzene (ppm) in Water leaving Vadose Zone
4 foot thick vadose zone
Loading to Groundwater
Vadose Zone Cleanup
Benzene Content in Vadose Zone
10.0
7.5
5.0
2.5
0.0
1980
1990
2000
2010
2020
2030
2040
2050
2060
2070
2080
Date


1997--Benzene in Shallow Ground Water (ug/L, normalized)
Combination of February and October 1997 data.
Wells with free product assigned 3000 ug/L, unless data available.
Benzene in Ground Water
ug/L 1 500 1000 2000 3000
MW-1 0
MW-13 0
MW-12 3000
MW-3 0
MW-2 38
MW-21 3000
MW-22 3000
MW-20 237
MW-10 0
MW-14
MW-15
MW-19 1225
MW-23 26
MW-4 0
MW-9 3000
MW-18 532
MW-17 300
MW-5 0
MW-16V 3000
MW-26 153
MW-7 2250
ORW
MW-8 2700
27
PZ-3 421
PZ-5 654
PZ-4 2500
PZ-24 3000
PZ-23 300
PZ-1 0
PZ-18 0
PZ-27 0
PZ-25 3000
PZ-29
PZ-8 712
PZ-26 1750
PZ-8 484
PZ-9 3000
MW-2 1060
PZ-28 0
PZ-12 625
PZ-11 30
PZ-22 0
PZ-14 0
PZ-15 0
PZ-13 0
PZ-16 0
PZ-17
PZ-19 0
PZ-20
RW-8
RO-1
0 500 1000 1500 2000 2500 3000 3500 4000 4500 5000 5500 6000 6500 7000
1000 1500 2000 2500 3000 3500 4000 4500 5000 5500 6000 6500

## Calculation of benzene removal rate from smear zone by transport & biodegradaton in GW

**Estimated quantities of BTEX in smear zone soil for strip 1 foot wide through contaminated soil (1976)**

3300 feet long strip - 5 feet in saturated zone - 5 feet in unsaturated zone

TPH = 14,000 ppm - B = 0.6% TPH - T = 2.4% TPH - E = 0.6% TPH - X = 2.7% TPH

| | | | | | |
|---|---|---|---|---|---|
| Benzene | 142,860 | gm | BTEX | 1,500,026 | gm |

**Estimated flow of groundwater through 1 foot wide strip smear zone (5 feet thick) and aquifer (14 feet thick)**

| | | | | |
|---|---|---|---|---|
| Hydraulic conductivity | 220 | ft/day | | |
| Hydraulic gradient | 0.00375 | ft/ft | | |
| Porosity | 0.25 | | | |
| Groundwater Flow Rate | 1,205 | ft/year | 34,130 | Kg/year |
| Volume Flow - Smear | 1,507 | cu.ft./year | 42,663 | Kg/year |
| Volume Flow - Aquifer | 4,219 | cu.ft/year | 119,455 | Kg/year |

**Estimated flow of electron acceptors into 1 foot wide strip upgradient of smear zone**

| Electron Acceptor | Concentration | Units | Flow Rate | Units | Comment |
|---|---|---|---|---|---|
| Sulfate | 39 | mg/L | 991.2 | gm/year BTEX equiv | 4.7 gm sulfate = 1 gm BTEX |
| Nitrate | 2 | mg/L | 48.8 | gm/year BTEX equiv | 4.9 gm nitrate = 1 gm BTEX |
| Oxygen | 8 | mg/L | 304.3 | gm/year BTEX equiv | 3.14 gm oxygen = 1 gm BTEX |

**Esitmated flow of electron donors out of 1 foot wide strip downgradient of smear zone**

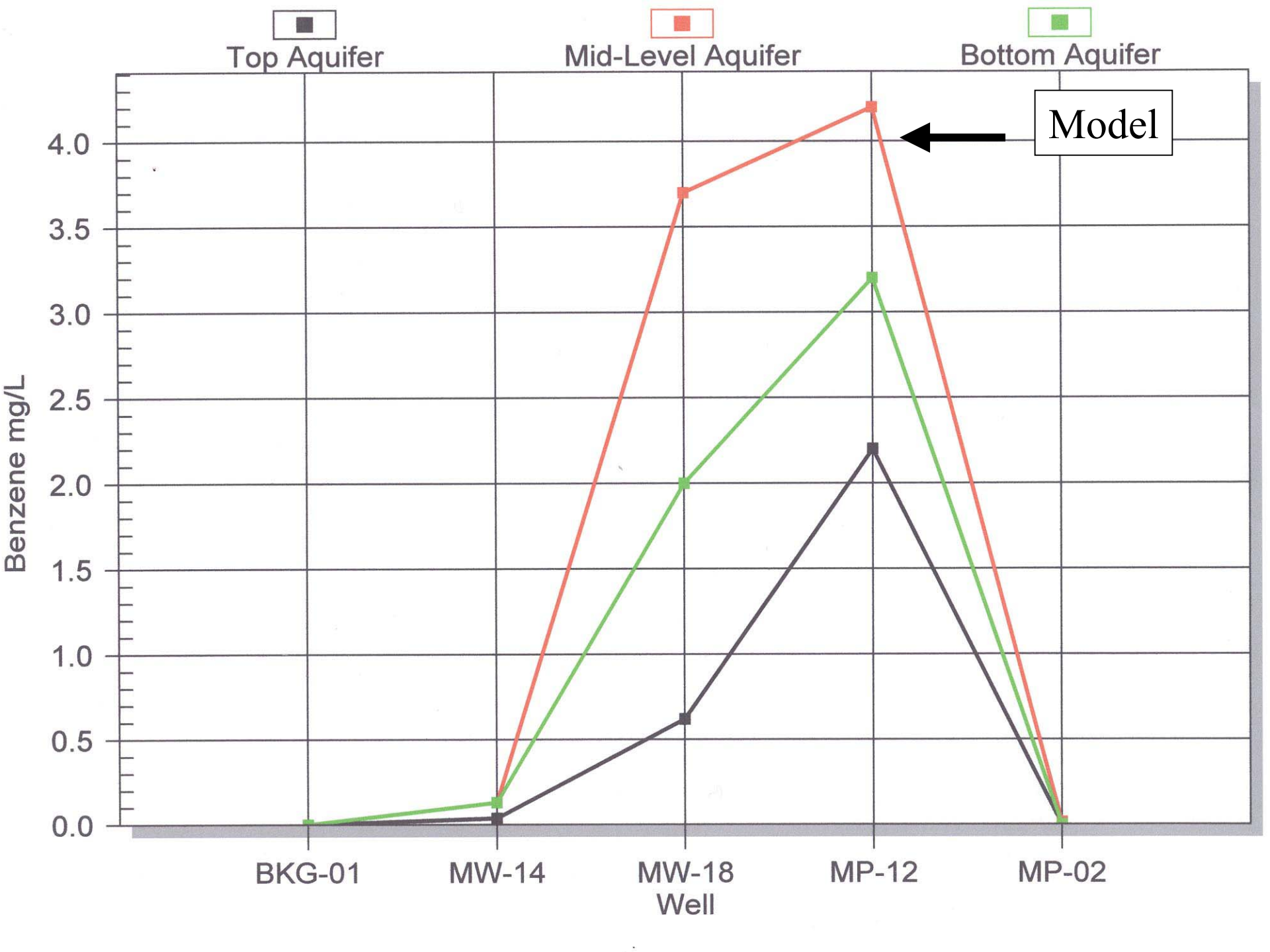
| Electron Donor | Concentration | Units | Flow Rate | Units | Comment |
|---|---|---|---|---|---|
| Methane | 15 | mg/L | 2297.2 | gm/year BTEX equiv | 0.78 gm methane = 1 gm BTEX |
| Ferrous | 13 | mg/L | 71.2 | gm/year BTEX equiv | 21.8 gm ferrous = 1 gm BTEX |
| Benzene | 4 | mg/L | 170.7 | gm/year | flow rate through smear zone |

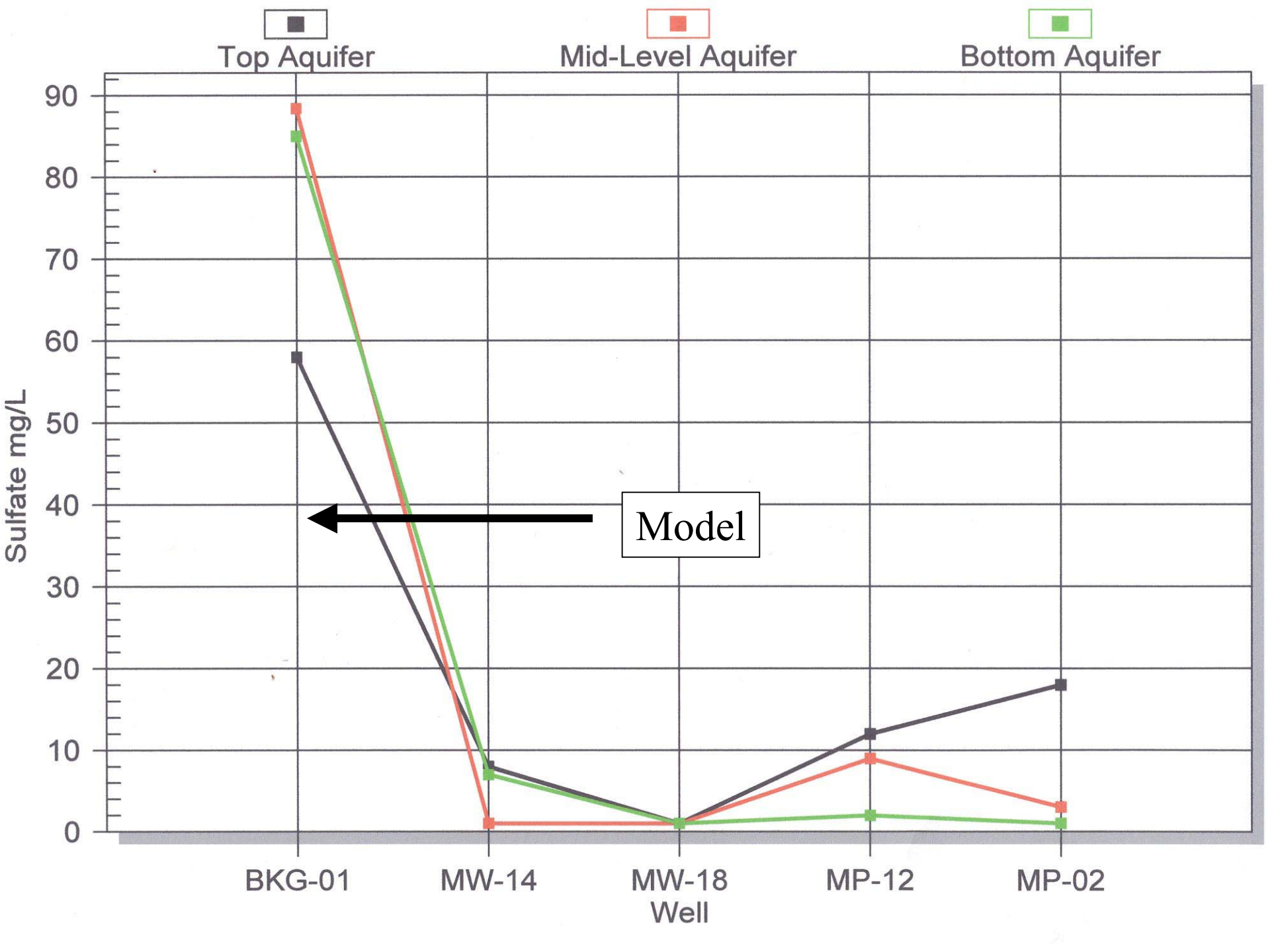
**Estimated timeframe for Benzene Cleanup**

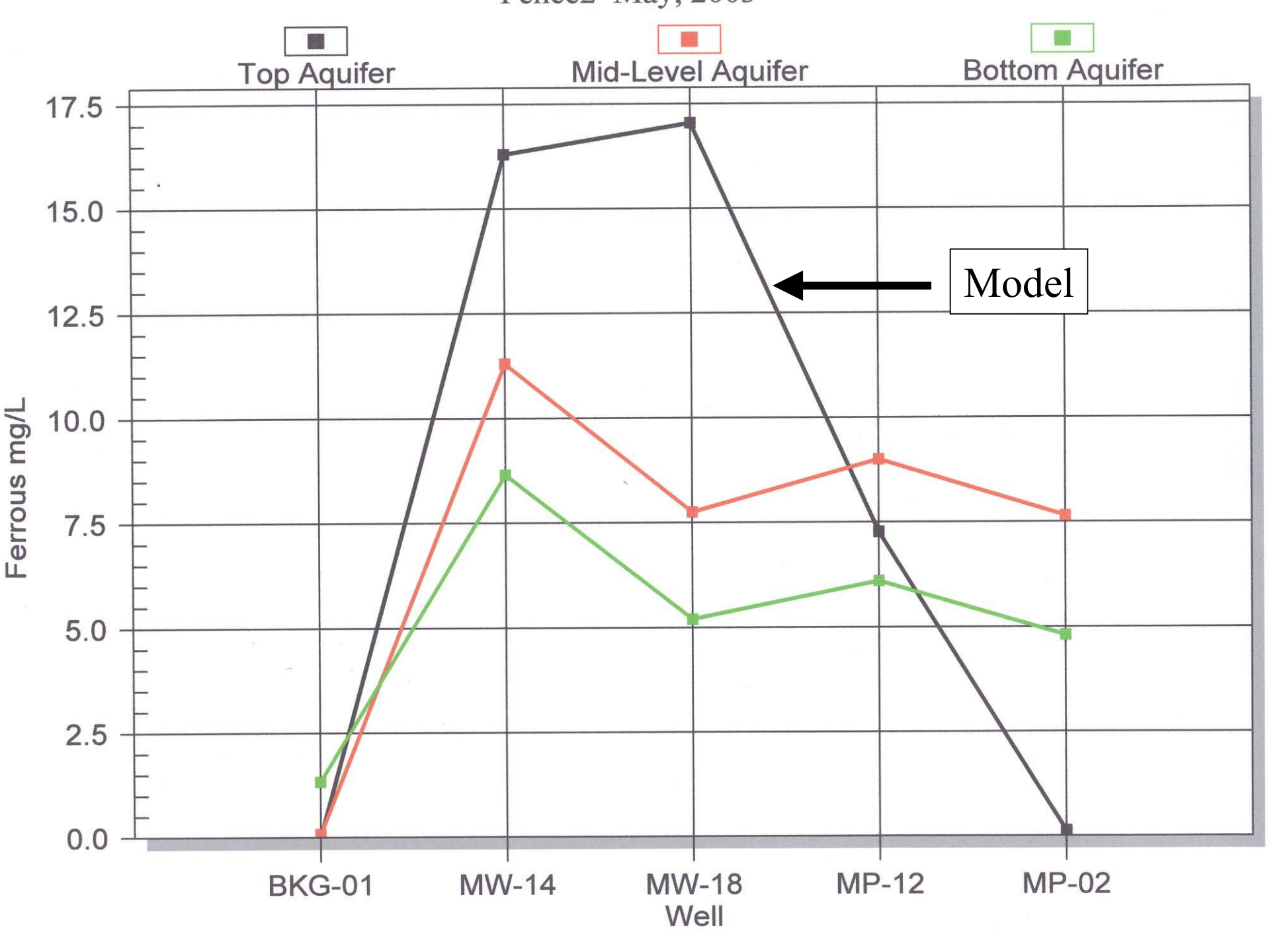
| | | |
|---|---|---|
| **Benzene Removal into Downgradient Plume** | **837** | Years Since Start (1976) |
| **Add Biodegration - Electron Acceptors** | **94** | Years Since Start (1976) |
| **Add Biodegradation - Electron Donors** | **37** | Years Since Start (1976) |
| **BTEX - all processes** | **386** | Years Since Start (1976) |

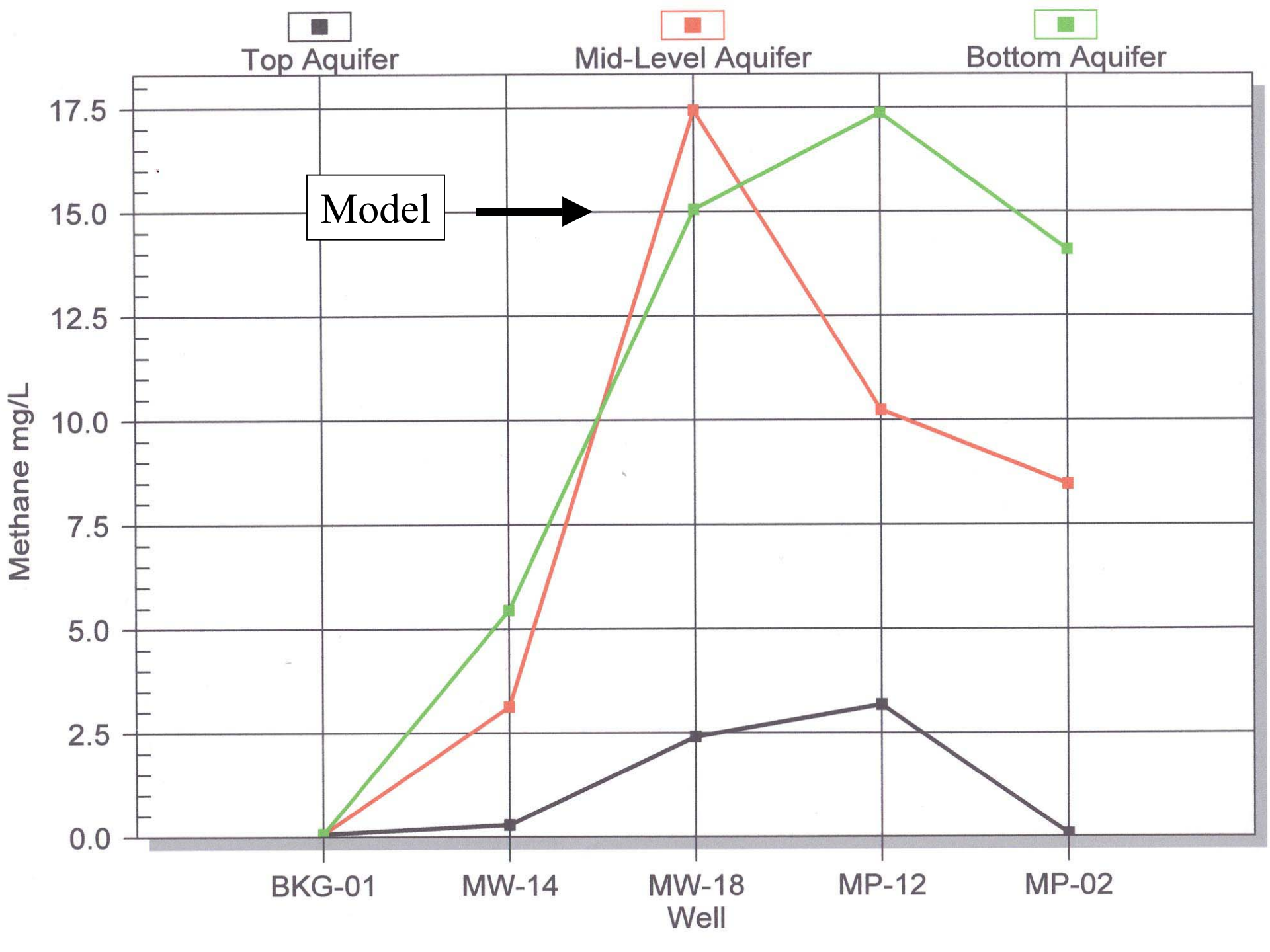
# Groundwater Model

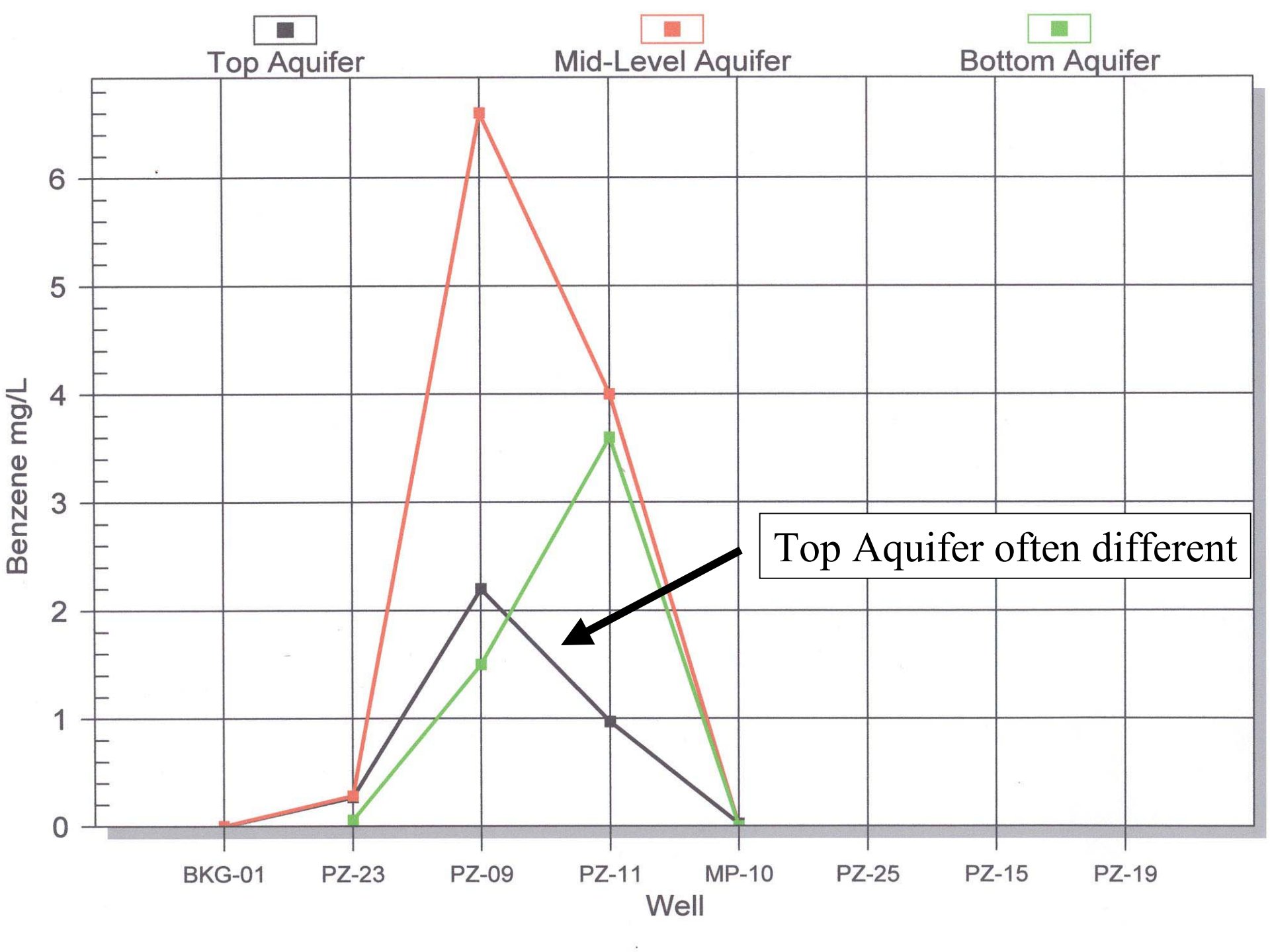
- Collect groundwater samples along vertical profiles in groundwater.
  - Upgradient, within smear zone area, downgradient
  - Measure contents of O2, NO3, SO4, Ferrous, CH4, BTEX
- Compare field data to concentration values used in model
  - Modify model input parameters
- Add input of BTEX to groundwater from vadose zone
  - Rate vs time obtained from Percolation Water model
- Allow for degradation of TEX and other soluble TPH
- Evaluate additional processes documented by field data
  - Volatile loss of methane and H2S
  - Recycling of SO4

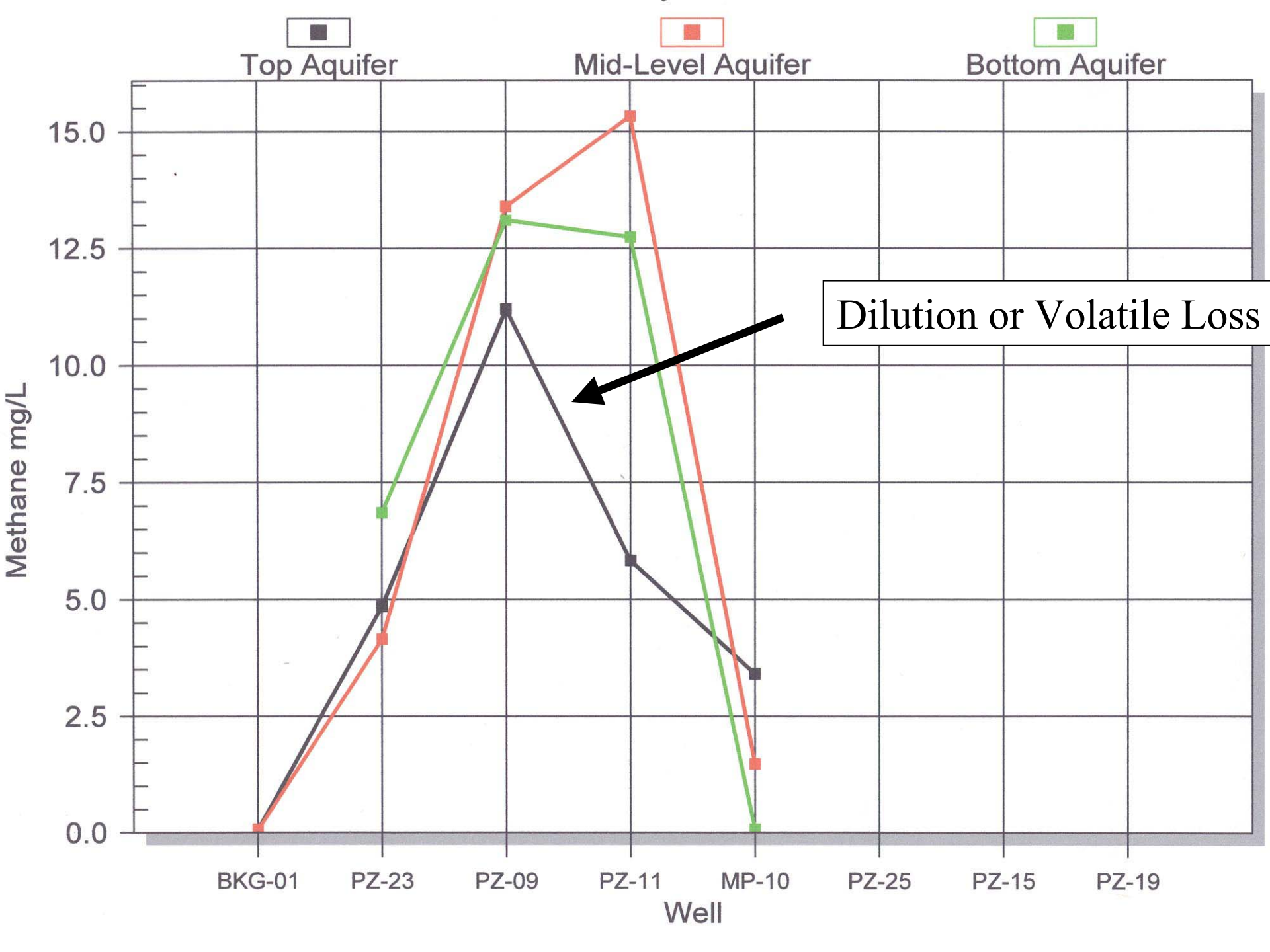

Top Aquifer
Mid-Level Aquifer
Bottom Aquifer
Model
Benzene mg/L
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
BKG-01
MW-14
MW-18
MP-12
MP-02
Well

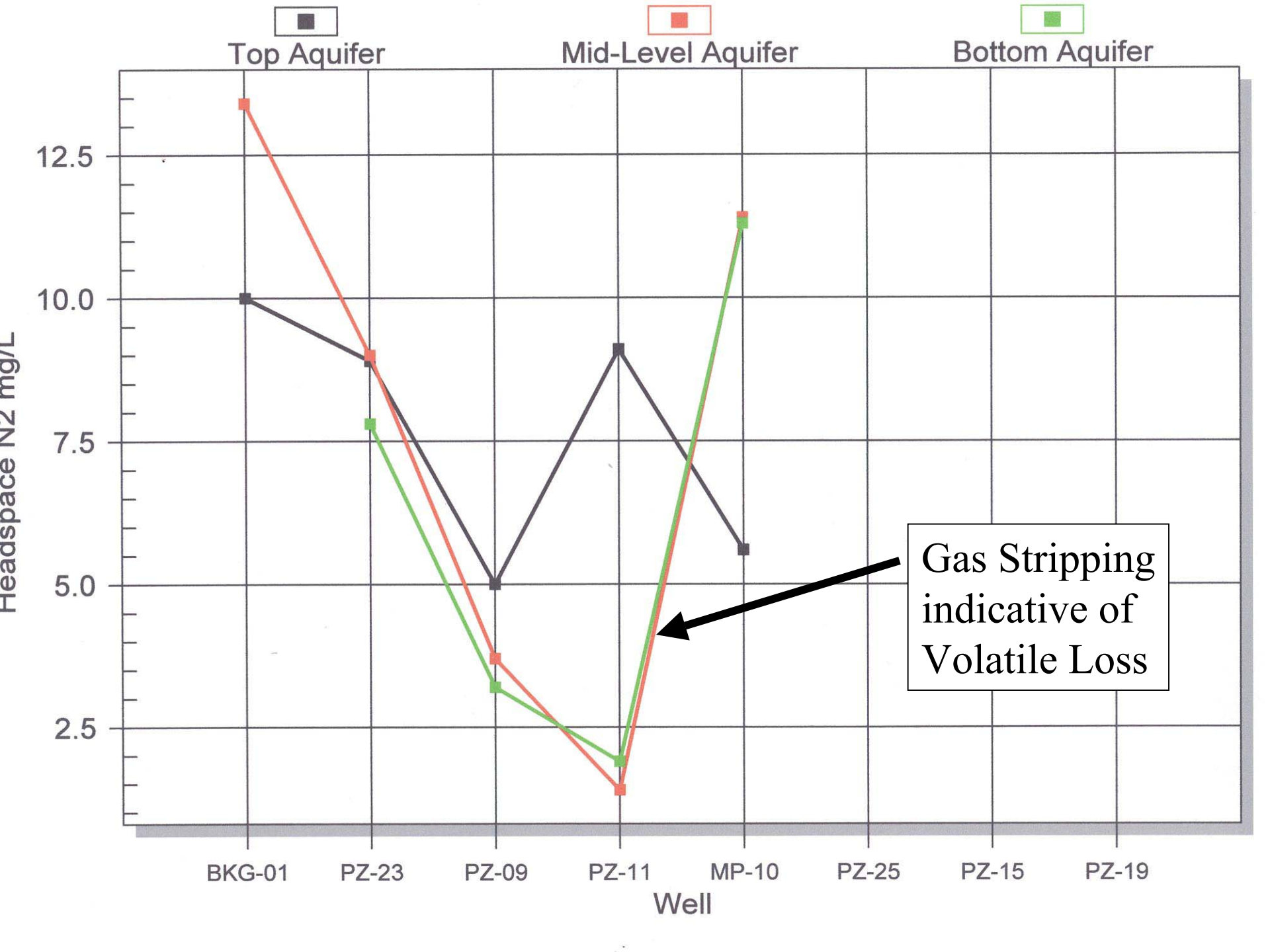

Top Aquifer
Mid-Level Aquifer
Bottom Aquifer
90
80
70
60
50
40
30
20
10
0
Sulfate mg/L
Model
BKG-01
MW-14
MW-18
MP-12
MP-02
Well

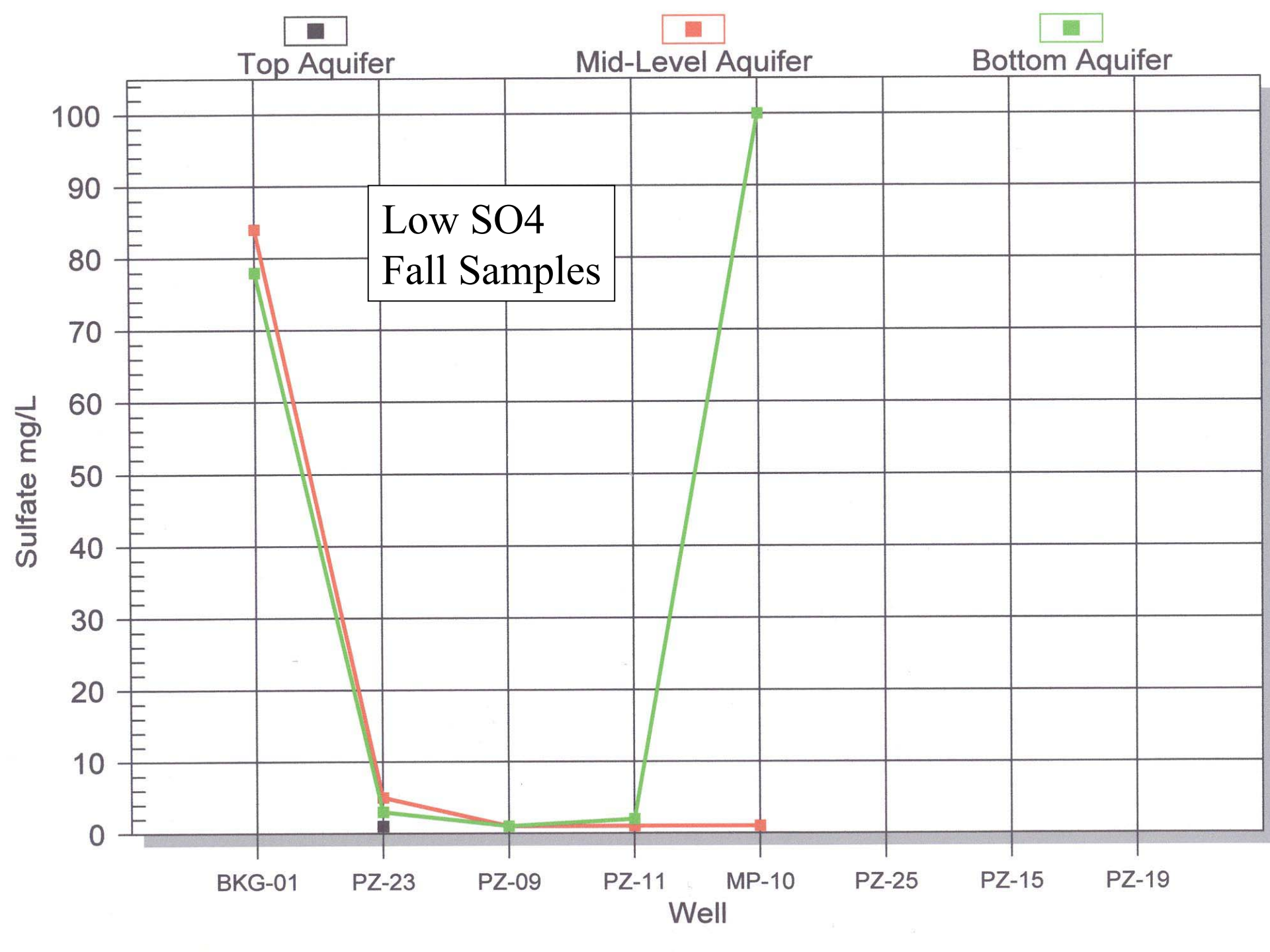

Top Aquifer
Mid-Level Aquifer
Bottom Aquifer
17.5
15.0
12.5
10.0
7.5
5.0
2.5
0.0
Ferrous mg/L
Model
BKG-01
MW-14
MW-18
MP-12
MP-02
Well

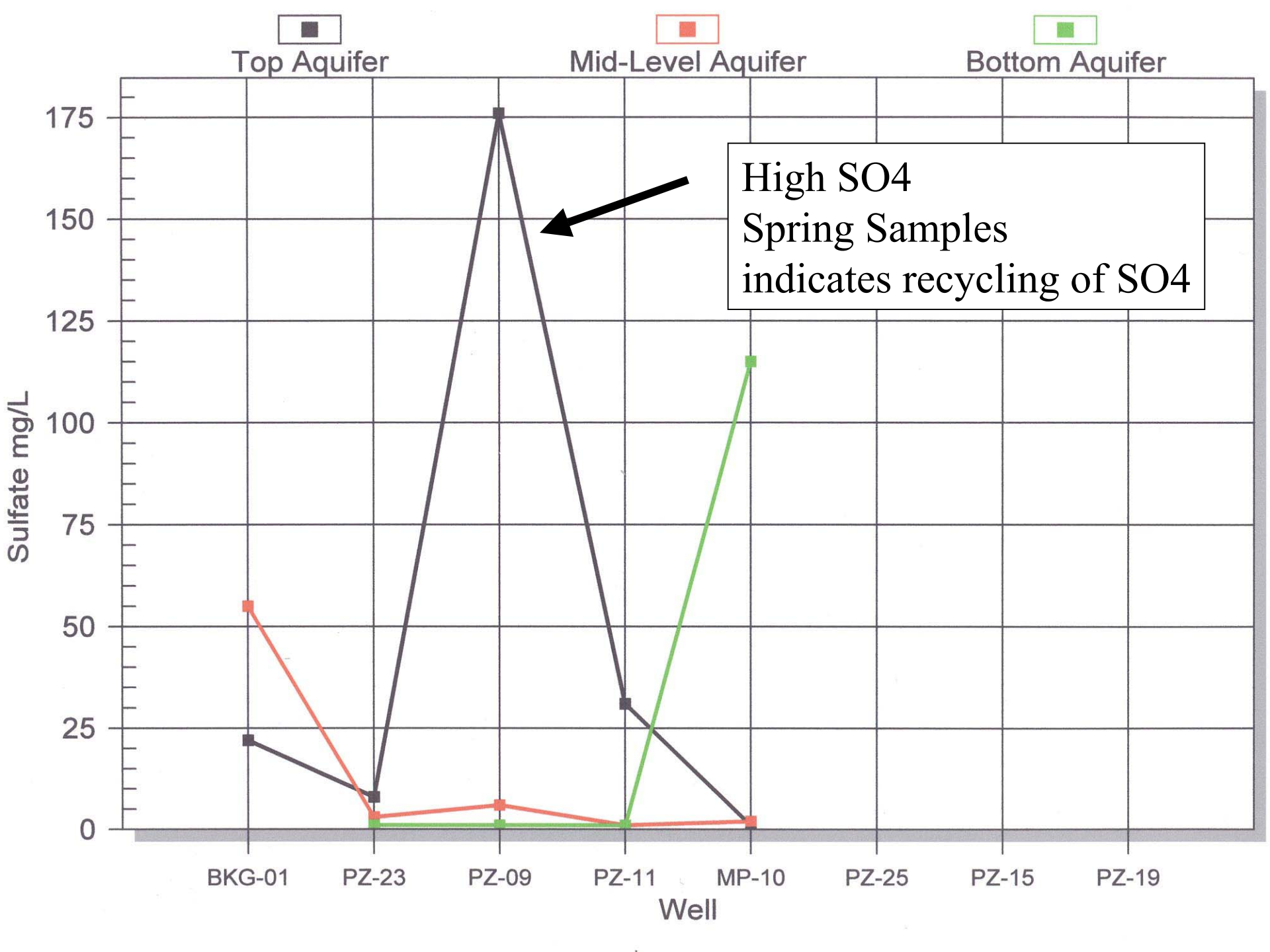

Top Aquifer
Mid-Level Aquifer
Bottom Aquifer
Model
17.5
15.0
12.5
10.0
7.5
5.0
2.5
0.0
Methane mg/L
BKG-01
MW-14
MW-18
MP-12
MP-02
Well


Top Aquifer
Mid-Level Aquifer
Bottom Aquifer
Benzene mg/L
0
1
2
3
4
5
6
BKG-01
PZ-23
PZ-09
PZ-11
MP-10
PZ-25
PZ-15
PZ-19
Well
Top Aquifer often different


Top Aquifer
Mid-Level Aquifer
Bottom Aquifer
15.0
12.5
10.0
7.5
5.0
2.5
0.0
Methane mg/L
Dilution or Volatile Loss
BKG-01
PZ-23
PZ-09
PZ-11
MP-10
PZ-25
PZ-15
PZ-19
Well


Top Aquifer
Mid-Level Aquifer
Bottom Aquifer
12.5
10.0
7.5
5.0
2.5
Headspace N2 mg/L
BKG-01
PZ-23
PZ-09
PZ-11
MP-10
PZ-25
PZ-15
PZ-19
Well
Gas Stripping indicative of Volatile Loss


Top Aquifer
Mid-Level Aquifer
Bottom Aquifer
Low SO4
Fall Samples
Sulfate mg/L
100
90
80
70
60
50
40
30
20
10
0
BKG-01
PZ-23
PZ-09
PZ-11
MP-10
PZ-25
PZ-15
PZ-19
Well


Top Aquifer
Mid-Level Aquifer
Bottom Aquifer
175
150
125
100
75
50
25
0
Sulfate mg/L
High SO4
Spring Samples
indicates recycling of SO4
BKG-01
PZ-23
PZ-09
PZ-11
MP-10
PZ-25
PZ-15
PZ-19
Well

# MNA Program

- Soil, Soil Gas, and Groundwater profiles collected in 2001
  - Chosen locations - permanent points used for soil gas and groundwater samples.
- Semi-annual collection of groundwater data for 2 years
  - Evaluate data to determine seasonal variations
  - Finished - no need to continue collecting semi-annual data
- Annual collection of groundwater data for 5 years
  - Use data to modify model and make cleanup projections
    - Evaluate different parts of site instead of site as whole
- Collect Soil and Soil Gas profiles in 2006
- Decision to continue will be based on field results